

SUPPORTED NOBLE METAL NANOMETER CATALYST PARTICLES CONTAINING CONTROLLED (111) CRYSTAL FACE EXPOSURE

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Field of the Invention

This invention relates to supported nanometer-sized catalytic crystal particle compositions of noble metals wherein the exposed faces of the nanometer-sized catalyst particles comprise predominantly crystal planes of the (111) type. The invention further relates to the method of preparing the nanometer-sized catalyst particles having predominantly (111) crystal planes as well as to the discovery of the particularly efficacious properties of these noble metal nanometer-sized particles in the catalysis of reactions such as hydrogenation, dehydrogenation and fuel cell applications

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Background of the Invention

In commercial practice, a large number of chemical transformations are accomplished using heterogeneous catalysts where the active component of the catalyst is a metal, often deposited on a support material. An important class of catalysts are those which utilize noble metals including the platinum group of metals (platinum, palladium, rhodium, ruthenium, iridium, and osmium) as well as silver, gold and rhenium. In comparison to other catalytic materials, the noble metals often have especially high activity and selectivity and are, therefore, frequently preferred over other catalyst materials.

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Because of their ability to facilitate the dissociative adsorption, surface reaction, and recombination/desorption of hydrogen, noble metals can catalyze a wide range of commercially important reactions, particularly the transfer, reaction or activation of hydrogen. These reactions and associated processes include various hydrogenations and related reactions such as methanation, carbonylation, hydroformylation, reductive alkylation, amination, hydrosilation, ammonia synthesis,

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oil or fat hardening and the like. Noble metal catalysis is also particularly useful in dehydrogenation reactions such as catalytic reforming, dehydrohalogenation reactions, steam reforming, partial oxidation and the production of gases including synthesis gas, hydrogen, carbon monoxide, carbon dioxide and the like. Noble metals are also used in important electrochemical processes such as fuel cell applications to carry out the dissociative adsorption of hydrogen and oxygen on the noble metal electrode, leading to the reaction of hydrogen with oxygen and the production of an electric current and by-product water.

Despite their wide-ranging effectiveness in catalytic chemical processes, noble metal catalysts have critical liabilities as the catalyst of choice for commercial chemical operations. Noble metals are extremely high cost and high catalyst attrition rates in a given chemical process can negate the choice of noble metals as a preferred catalyst for that process. Their high cost also requires that their superior catalytic activity be sufficiently high compared to other catalyst choices to justify their use. To ameliorate the cost disadvantage, those skilled in the art can employ noble metals catalyst as small particles whereby the overall efficiency of the catalyst is improved. This results in the greatest exposure of active noble metal surface areas for a given loading and offers the greatest noble metal utilization.

Nevertheless, even when methods are available to produce very small particles to improve efficiency and control catalyst costs, these particles are often unstable. The high surface energy of the small particles tends to cause migration and agglomeration of the metal particles such that a catalyst which initially comprises very small particles and high noble metal surface area can lose surface area. Improved methods are needed to prevent this migration and agglomeration of catalyst particles.

Another critical problem associated with noble metal catalysis is catalyst leaching by dissolution of noble metal into the surrounding liquid reaction medium. Because of the high cost of noble metals, leaching can be a very costly burden on

overall process economics as it leads to a loss of catalyst efficiency and necessitates an enhanced catalyst recovery process. Typical noble metal catalysts are known to have leaching rates of 5-10% per year or higher; that represents a substantial economic burden on any catalytic process. Accordingly, those skilled in the art have long sought improved methods to anchor noble metal particles on substrate surfaces in smaller particle sizes that will neither agglomerate nor experience prohibitive catalyst leaching rates.

Yet another problem with the current state-of-the-art for noble metal catalysts is the inability to properly control the active site distribution on the catalytic surface. For any particular catalyzed reaction, it is known that only certain types of surface active sites are, indeed, catalytically active and preferred for the selected catalyzed reaction. A key determining locus that defines the controlling characteristics of the surface active sites is the noble metal crystal face. Small metal crystals generally expose mainly low-order crystal faces, such as (100), (110), and (111). Normally, the most desired active sites for a given reaction are on only one of these faces so that a catalytically very active catalyst particle would be one that preferably contains a preponderance of that particular active crystal face. Unfortunately, prior art catalyst manufacturing methods produce catalysts containing crystal faces having a mixture of all of these preferred and non-preferred crystal faces. This reduces the efficiency of noble metal utilization and can also lead to non-selective reactions that are catalyzed by the non-preferred active sites on the crystal face. Therefore, the utility and efficiency of noble metal catalysts would be improved by introducing catalyst preparation methods that control the distribution of the crystal face exposition of noble metal particles to favor those configurations most effective in catalyzing the selected reaction.

Summary of the Invention

Addressing the aforementioned problems to overcome them and provide an improved catalyst for selected types of reactions has led to the discovery that

supported nanometer scale noble metal particles containing a preponderance of (111) type of crystal phase upon the crystal face of the catalyst particles are especially effective catalysts for reactions that fall within the general classes of hydrogenation or dehydrogenation reactions, including half-cell electrochemical reactions as carried out in hydrogen/oxygen fuel cells for the independent production of electricity. The support material for the noble metal catalyst is preferably a porous material such as porous alumina or carbon black .

The invention provides both an improved supported noble metal catalyst comprising nanometer scale particles applicable to selected reactions and a method for producing the improved catalyst. The particles of the invention preferably comprise noble metal particles of less than 5 nanometers, more preferably less than 2 nanometers. An especially important aspect of the invention is the discovery that the most effective crystal face of the noble metal particles useful in the selective reactions have a predominant exposure of the (111) type of crystal phase. Yet another important aspect of the invention is the finding that the nanometer scale noble metal particles are anchored to the surface of a supporting substrate in a way that prevents their subsequent migration and agglomeration. As a consequence of these properties, the catalyst of the invention is advantageously useful over the prior art for many important catalytic reactions. Depending on the application or reaction-type, these advantages include: (a) a higher activity derived from the increased noble metal surface areas of the extremely small crystallites containing the selective exposure of predominantly the (111) type of crystal phase upon the noble metal faces; (b) higher selectivity due to the selective exposure of the (111) type of crystal phase upon the noble metal crystal faces, (c) an improved catalytic stability and life due to the anchoring of the noble metal crystallites.

The method preparing the supported noble metal catalyst having nanometer-sized crystal particles with a preponderance of (111) type of crystal phase on the face of the noble metal particles includes the steps of:

preparing a solution of a noble metal salt and a metallo-organic sequestering agent;
treating the solution of sequestered noble metal with a reducing agent;
impregnating a catalyst support with the reduced noble metal solution;
5 drying the impregnated support; and
activating the catalyst by reducing the dried impregnated support to yield the nanometer-sized noble metal catalyst having a preponderance of 111 type of crystal phase on the face of the noble metal particles.

10 Depending on the metallo-organic sequestering agent employed to prepare the initial sequestered noble metal solution, treatment of the solution with a reducing agent in a second step may not be necessary and the noble metal sequestered solution may be used directly to impregnate the catalyst support prior to activation. Generally, before impregnating the catalyst support material, in the
15 process of the invention it is not necessary to hydrogenate sequestered noble metal solutions prepared by reaction with small molecule metallo-organic sequestering agents.

20 As to the types of catalytic reactions to which the catalyst of the invention can be applied, hydrogenation is a preferred choice and includes the full scope of hydrogenation reactions as applied to acyclic and cyclic olefinic compounds, carbonyls, aromatic compounds, and oxides of nitrogen, sulfur, phosphorous, carbon and the like. Applicable catalytic dehydrogenation reactions especially include reforming of naphtha, cyclization of aliphatic compounds and alkane
25 dehydrogenation to form alkenes. The catalyst is also useful in steam reforming of hydrocarbons, partial oxidation and the like.

Description of the Figures

30 Figures 1a, 1b and 1c depict the atomic surface structure (110, 100 & 111) of different crystal phases of noble metal catalyst surfaces (Pt).

Detailed Description of the Invention

Applicants' issued patent U.S. 6,168,775 B1, incorporated herein by reference in its entirety, is instructive for the reader as to the significant role the crystal phase exposition (110) of a noble metal catalyst can assume in determining the selectivity of a chemical reaction, e.g., hydrogen peroxide formation from hydrogen and oxygen reactants, even over the thermodynamically favored selectivity of water as the end-product of the reaction. Pursuing this insight further into the phenomena of noble metal catalysis of hydrogen-based reactions, applicants have discovered that when the geometry of the crystal surface of a noble metal catalyst particle is controlled to present a (111) crystal plane, i.e., a plane wherein each metal atom on the surface is surrounded by six other metal atoms, the catalyst is highly selective for the propagation of certain reactions including hydrogenation, dehydrogenation, partial oxidation and the like.

Referring to Figures 1a-1c, the distinction of applicants' discovery is illustrated. Applicants' have discovered that, although the chemical composition of the noble metal catalysts depicted in Figures 1a-1c is identical, the differing crystallographic structures of the active catalyst surface of 1a-1c play a determining role in establishing the comparative effectiveness or selectivity of the catalyst for different types of hydrogen-based reactions. Whereas, in U.S.6,168775B1 crystal phase exposition (110) is selective for the formation of hydrogen peroxide from hydrogen and oxygen, the instant invention teaches that crystal phase exposition (111) is selective and preferable over (110) for hydrogenation and dehydrogenation reactions, among others.

However noteworthy the foregoing discovery of the special efficacy of crystal phase exposition (111) is for reductive reactions, absent a means to routinely and reliably prepare noble metal catalyst particles with a preponderance of (111) faces, the discovery would remain of academic interest, but also remain commercially sterile. Therefore, applicants have diligently bent themselves to the pursuit of economically reasonable methods for preparing noble metal catalyst particles with

the assigned exposition to convert their discovery to a practical commercial reality. They have discovered that by treating noble metal cations with select, small polyfunctional cation sequestering organic molecules or metal sequestering non-linear organic and inorganic oligomers, the resultant noble metal cationic complex can be deposited on a support material and converted, preferably by further reduction, to provide the supported noble metal crystalline nanometer-size particles of the invention containing a preponderance of the preferred (111) crystal face exposition. Preferably, acids such as glycolic acid are used to form the metallo-organic complex onto a catalyst support and reduced to yield the active noble metal catalyst of the invention.

The recovered catalyst of the invention, as described above, demonstrates both high selectivity and activity for the preferred reduction reactions. It is thought that the sizing of the noble metal catalytic particles in the nanometer range (< 5 nanometers) is the contribution largely responsible for the increase in catalytic activity since more catalytically active site are created. However, the concomitant and concurrent advantage of the catalyst in reaction selectivity must be assigned to applicants' discovery of the significant importance of establishing a preponderance of (111) type crystal planes on the catalytic face. The combination of both enhanced activity and high selectivity succeeds in distinguishing applicants' invention over prior art catalytic processes.

The conversion processes of the invention are conducted using a specially prepared phase-controlled supported noble metal catalyst from which the most important advantages of this process are derived. The catalyst consists of an inorganic oxide or carbon support holding nanometer-sized crystallites of one or more metal components, where the metal or metals normally include at least one noble (platinum-group) metal such as palladium, in combination with one or more of platinum, rhenium, rhodium, ruthenium, osmium, iridium, gold, or combinations thereof. Other metal constituents such as nickel, tin, copper, iron, and the like, may be included either individually or in combination. The amount of noble metal

constituents will typically be 0.01 to 10% of the total catalyst weight, but preferably 0.1 to 5% by weight. Other components may also be included in amounts of 0.01 to 20 % by weight, depending upon the selection and function of the additional component. These other components include transition metals, alkali metals, alkali earth's, rare earth's and non-metals.

The noble metal particles are deposited on carbon or inorganic metal oxide support, minerals, polymeric materials and the like. Examples of noble metal catalyst supports are activated carbon, carbon black, fluoridated carbon, alumina, bentonite, clay, diatomaceous earth, zeolite, silica, zirconia, magnesia, titania, and the like, and also mixtures of those. The support should preferably be a porous material having a surface area of more than 20 m²/g, and more preferably more than 50 m²/g, up to 500 m²/gm. Preferably, the support material comprises at least 90% by weight of the total catalyst weight. Any material that can serve as a useful support for a heterogeneous catalyst may be used as a support material for the catalyst of the invention.

The noble metal crystallites are preferably deposited on the substrate support material using a small molecule binding agent or sequestering agent such as glycolic acid and non-linear oligomeric metal sequestering agents which disperses the deposited metal into the desired nanometer-sized particles and strongly bonds the particles to the surface. It has been found that this controlled deposition method allows metal crystallites to be deposited with a high selectivity for exposing specific (111) metal crystal faces. It is believed that the (111) crystal face exposure is somehow favored by employing as a noble metal cation sequestering agent those chemicals that are relatively structurally unrestricted as to the form they can assume when deposited on the support material. When deposited, the sequestration complex on the substrate is activated by reduction with hydrogen. These several features of the metal deposition method produce a catalyst with properties that are highly advantageous for use in the application processes of the invention. The unique features include:

producing nanometer-sized particles which contributes to especially high catalyst activity;

controlled exposition of known metal crystal faces promotes the selectivity of the catalytic reaction toward the desirable products;

strong bonding of the metal crystallites to the substrate surface prevents agglomeration of metal particles into larger structures, which would cause the desirable high activity of the catalyst to be lost. Further, the strong bonding substantially prevents the attrition of the active metal components into the surrounding liquid medium during use of the catalyst.

The following exposition teaches the specific design and preparation of the catalyst of the invention as potentially applied to a preferred application - hydrocarbon reforming.

General Example 1 - Catalyst Design, Preparation & Application

Since catalytic reforming is essentially the breaking of carbon-hydrogen bonds to form carbon-oxygen and hydrogen-hydrogen bonds, the active catalyst should have a structure with active sites adjacent to each other in order to carry out the prescribed reaction of bond cleavage and exchange. Referring to Figure 1, it is observed that the platinum (Pt) crystal face (110) contains a structure wherein each Pt atom is surrounded only by two adjacent Pt atoms on the crystal surface layer. For the crystal face (100), each Pt atom is adjacent to 4 other Pt atoms. But for crystal face (111), each Pt atom is adjacent to 6 other Pt atoms. Accordingly, it is apparent that crystal face (111) will provide more active sites on the surface for breaking C-H bonds for reforming methane or other hydrocarbons. The adjacent characteristics of the sites of (111) will also improve the efficiency of the reforming reaction for recombining the adjacent hydrogen atoms to form hydrogen molecules and combining carbon plus oxygen from adjacent sites to form carbon oxide molecules, principally carbon monoxide.

To implement the findings of the preceding paragraph and achieve a more efficient hydrocarbon reforming process, a controlled dispersion method is used to prepare the requisite noble metal catalyst such as Pt having a catalyst particulate face abundant in type (111) crystal phase exposure. But to augment the advantages of the type (111) crystal phase exposure, the supported catalyst particles are prepared to exhibit catalyst particles of not greater than 5 nanometers in size, preferably not greater than 2 nanometers. A first step is the preparation of a solution of a Pt salt. The Pt salt is reacted with a control or binding agent to form an organo metallic complex with the noble metal. The control agent can be a small organic molecule containing at least two functional groups to sequester the Pt moiety. Functional groups such as OH or COOH are useful. Alternatively, the control agent can be a branched, cross-linked or non-linear sequestering ionic polymer or oligomer capable of binding with the Pt moiety. The control or sequestering agent used in the invention serves two functions: first, it binds or holds the Pt for deposition onto the catalyst; and secondly, the control agent also forms intermolecular hydrogen bonds with the support material to provide a network as a template base for Pt (111) phase formation. The holding structure of the control agents prevents Pt atoms from agglomerating to form large particles. Typically useful control agents include small molecules such as glycolic acid or citric acid and salts thereof. For polymeric control agents branched or cross-linked polyacrylic acid or their salts are useful.

The described controlled dispersion method produces a catalyst with nanometer-sized noble metal particles having a thin catalytic layer on the support surface.

Specific Example 2

For preparing a Pt catalyst having a (111) crystal phase surface a desired amount of platinum chloride is dissolved in water. A phase control agent solution such as glycolic acid solution is mixed with the platinum chloride solution in a ratio of metal

to agent between 1:0.5 and 1:10. The combined solution is purged with nitrogen and then reduced with hydrogen. The formed organo-metallic complex ,i.e., platinum glycolate is deposited on a catalyst support such as alumina by impregnation. The network of glycolate holds the Pt during impregnation to provide dispersion with a (111) crystal phase pattern. The obtained sample was dried in air and activated by a reduction in hydrogen at temperatures 100-400 degrees C. The result is a catalyst with Pt(111) crystal phase surface exposition. Preferably, the final catalyst has a Pt loading between 0.01 to 5% by weight; more preferably 0.01 to 1% by weight.

The catalyst of the invention is useful for the catalysis of a variety of chemical reactions. It can be used, for example, for the catalysis of hydrogenation reactions including hydrogenation of olefins, acetylenes, carbonyls, aromatics, carboxylic acids, anthraquinones, imines, nitriles, nitro and nitroso compounds, pyridines, carbon monoxide and carbon dioxide and the like.

The catalyst can also be useful for various dehydrogenation reactions including catalytic reforming of naphtha, cyclization and/or aromatization of aliphatic hydrocarbons, alcohol dehydrogenation. The catalyst can be used in steam reforming of hydrocarbons partial oxidation, and the like. Applicable feedstocks for these reactions and the catalyst of the invention include methane, gasoline, kerosene, diesel fuels, methanol and ethers. These reactions are useful for the production of synthesis gas and may be applied to applications such as fuel cells.

The catalyst of the invention can be used in any of a variety of practical reactor types, depending on the specific application. Any reactor type known to those skilled in the art can be used.